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(54) Title: STABILIZATION OF POLYETHYLENE POLYMERS

(57) Abstract

A method for stabilizing a polyethylene composition, such as a linear low density polyethylene, against degradation, by incorporating into the polyethylene composition, an effective stabilizing amount of a stabilizing composition of: (a) a pentaerythritol diphosphite; and (b) an antioxidant compound selected from the group consisting of: (i) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; (ii) at least one sterically hindered phenol; and (iii) a combination of (i) and (ii). Stabilized polyethylene compositions are also described which have the above-described stabilizing composition incorporated therein.

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STABILIZATION OF POLYETHYLENE POLYMERS

Field of the Invention

This invention relates to a method for stabilizing a polyethylene composition against degradation, which comprises incorporating into the polyethylene composition, a stabilizing composition comprising a pentaerythritol diphosphite, and at least one diphenylamine derivative and/or at least one sterically hindered phenol. In particular, this invention relates to a method for stabilizing linear low density polyethylene (LLDPE) against degradation, which comprises incorporating into the linear low density polyethylene, a stabilizing composition comprising a pentaerythritol diphosphite, and at least one diphenylamine derivative and/or at least one sterically hindered phenol.

This invention also relates to polyethylene compositions stabilized against degradation.

Background of the Invention

A long-standing problem of plastic goods manufacturers is stabilizing polyethylene resins during high temperature, high shear blending and extrusion processes which are common in plastic goods manufacturing. It has been found that resins that show excellent long-term thermal heat stability characteristics may not be sufficiently protected against the type of degradation which occurs in an extruder during long residence times.

In the production of linear low density polyethylene (hereinafter also referred to as "LLDPE"), various antioxidants, stabilizers, and additives are added to the raw polymer to prevent oxidation, discoloration, and thermal degradation during melt processing.

Compositions of certain antioxidants, including organic phosphites, have been described as useful for the

stabilization of polyethylene polymers. U.S. Patent No. 4,187,212 describes the use of a stabilization system consisting of triarylphosphite and a phenolic antioxidant, for stabilizing polyolefins. U.S. Patent No. 4,837,259 describes the use of an antioxidant composition consisting of an amine and a phenol, to stabilize polypropylene. U.S. Patent No. 5,096,590, describes the use of a composition containing hindered amines and phenolic stabilizers, for stabilizing polyolefins. Great Britain Patent No. 2,252,324A describes a composition containing a phenolic or amine antioxidant, a metal deactivator, and a neutralizer and/or a phosphorous-containing antioxidant, for stabilizing polyolefins. U.S. Patent No. 5,155,153 describes a stabilizing composition for thermoplastic organic polymers consisting of a hindered phenol, a triaryl phosphite, and a dialkylthiodipropionate. U.S. Patent 5,526,333, describes a stabilizing composition consisting of 3-component mixture of a diphenylamine, a hindered phenol, and a pentaerythritol diphosphite, useful as an additive for polyether polyols.

It is the purpose of this invention to provide a novel method for stabilizing polyethylene compositions, particularly LLDPE, against degradation, which comprises incorporating into the polyethylene compositions, a stabilizing composition comprising a pentaerythritol diphosphite, and at least one diphenylamine derivative and/or at least one sterically hindered phenol.

It is also the purpose of this invention to provide a novel polyethylene composition stabilized against degradation.

Summary of the Invention

This invention relates to a method for stabilizing a polyethylene composition against degradation, which comprises incorporating into the polyethylene

composition, an effective stabilizing amount of a stabilizing composition which comprises:

(a) a pentaerythritol diphosphite; and

(b) an antioxidant compound selected from the group consisting of:

(i) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine;

(ii) at least one sterically hindered phenol; and

(iii)a combination of (i) and (ii).

Preferably, the stabilizing composition in the method of this invention comprises:

a) a pentaerythritol diphosphite;

b) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; and

c) at least one sterically hindered phenol.

The method of the present invention protects the polyethylene composition against the adverse effects of actinic, oxidative and thermal degradation by substantially reducing the discoloration and other degradative effects which result from the processing of the polyethylene composition.

For the purposes of this invention, the term "polyethylene composition" means a composition which comprises one or more polyethylene homopolymers, polyethylene copolymers, or blends of homopolymers and copolymers. Preferred polyethylene compositions comprise LLDPE.

This invention also relates to a polyethylene composition stabilized against degradation, comprising:

(a) a polyethylene composition; and

(b) an effective stabilizing amount of a stabilizing composition comprising:

(i) a pentaerythritol diphosphite; and

(ii) an antioxidant compound selected from the group consisting of:

(1) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine;

(2) at least one sterically hindered phenol; and

(3) a combination of (i) and (ii).

Preferably, the polyethylene composition comprises an effective stabilizing amount of a stabilizing composition comprising:

a) a pentaerythritol diphosphite;

b) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; and

c) at least one sterically hindered phenol.

The term "effective stabilizing amount" is intended to signify that amount of the stabilizing composition necessary to stabilize the polyethylene composition for performance in actual use. The effective stabilizing amount of the stabilizing composition will vary depending upon the polyethylene composition used, but, in general, will be within the range of about 0.01 to 5.0% by weight of the polyethylene composition, and, preferably, from about 0.05 to 0.5% by weight of the polyethylene composition.

Detailed Description of the Invention

In a preferred embodiment, this invention is directed to a method for stabilizing a linear low density polyethylene compostion against degradation which comprises incorporating into the LLDPE composition, an effective stabilizing amount of a stabilizing composition which comprises:

(a) a pentaerythritol diphosphite; and

(b) an antioxidant component selected from the group consisting of:

(i) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine;

(ii) at least one sterically hindered phenol; and

(iii)a combination of (i) and (ii).

An LLDPE composition comprising the stabilizing composition has been found to be protected against degradation to a significantly greater degree than the LLDPE composition alone or the LLDPE composition comprising any of the components of the stabilizing composition separately. The use of the stabilizing composition yields a polymer with minimal color formation after multiple extrusions. As can be seen below in Tables 1 and 2, the retardation of discoloration in the finished polymer stabilized with the stabilizing composition of the method of this invention represents a substantial improvement over other single and multi-component stabilizer compositions.

The improved stabilization is also evidenced by the melt viscosity data presented in Tables 1 and 2. The melt viscosity data indicates the uniformity of the flow rate of the polymer and is indicative of uniformity of other properties, as will be described below.

The diphenylamines, hindered phenols and pentaerythritol diphosphites that are employed in the stabilizing composition of the method of this invention are individually well known compounds.

The pentaerythritol diphosphites that can be utilized in the stabilizing composition of this invention are preferably the sterically hindered bis(aryl)-pentaerythritol diphosphites, numerous examples of which are known in the art. See, e.g., U.S. Patents Nos. 2,847,443, 4,302,383, 4,305,866, and 4,692,539. Of these

diphosphites, those in which the aryl groups are substituted with alkyl groups from about 1 to about 20 carbon atoms are particularly preferred. The aryl groups are preferably phenyl groups and contain branched alkyl groups in the 2 and 4 positions relative to one another on the phenyl ring. An example of such a phosphite is distearyl pentaerythritol diphosphite.

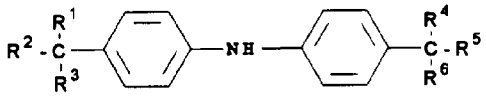
An especially preferred pentaerythritol diphosphite for use in the instant invention is bis(2,4-di-t-butylphenyl)pentaerthrytol diphosphite (BPD), which is available under the tradename Ultranox 626 (General Electric Specialty Chemicals). This compound can contain approximately 1 weight percent of triisopropanolamine to add hydrolytic stability to the diphosphite.

BPD is a high performance solid organophosphate antioxidant which is known for its stabilization of polyolefins, polyesters, styrenes, engineering thermoplastics, polyvinyl chlorides, elastomers and adhesives.

The pentaerythritol diphosphite component will generally be present in amounts from about 30 to about 70, preferably, from about 40 to about 60, and, most preferably, from about 45 to about 55, weight percent based on the entire weight of stabilizing composition.

Pentaerythritol diphosphites are more effective for use in the antioxidant composition of this invention than other phosphites currently in use as additives in the manufacture of polymeric materials. Examples of such other phosphites are tris (nonylphenyl) phosphite, phenyl diisodecyl phosphite, tris (2,4-di-t-butylphenyl) phosphite, tridecyl phosphite and triisooctyl phosphite.

Representative diphenylamines useful in the composition of this invention have the formula



wherein R^1 and R^4 are hydrogen, C_1-C_4 alkyl or phenyl, preferably phenyl; and R^2, R^3, R^5 and R^6 are hydrogen or C_1-C_4 alkyl, preferably methyl. A preferable diphenylamime that can be employed in this compostion is 4,4'-bis(α,α-dimethylbenzyl)-diphenylamine, also known as Naugard 445®(Uniroyal Chemical Company, Inc.). The amount of diphenylamine in the stabilizing composition useful in this invention can vary, e.g., from about 10 to about 70, preferably from about 20 to about 60, and most preferably from about 20 to about 30, weight percent based on the entire weight of stabilizing composition.

Suitable hindered phenols that can be utilized in the stabilizing composition herein include 2,4-dimethyl-6-octylphenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-nonylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-n-butylphenol, 2,6-di-t-butyl-4-sec-butylphenol, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 2,4-dimethyl-6-t-butylphenol, 4-hydroxymethyl-2,6-di-t-butylphenol, n-octadecyl-β(3,5 di-t-butyl-4-hydroxyphenyl)propionate, 4,4'-dihydroxydiphenol, 4,4'-thiobis(6-t-butyl-o-cresol), and mixtures thereof. A preferred hindered phenol is octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, which is commercially available under the tradename Naugard 76 (Uniroyal Chemical Company, Inc.) Other preferred hindered phenols include tetrakis [methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] methane and 2,2'-oxamidobis(ethyl)-3(3,5-di-t-butyl-4-hydroxyphenyl)propionate, which are commercially available under the tradenames Naugard 10 and Naugard XL-1 (both trademarks of the Uniroyal Chemical Company,

Inc.)

The hindered phenol component of the stabilizing composition useful in the method of this invention can be present therein in widely varying amounts, e.g., from about 10 to about 70, preferably from about 20 to about 60, and most preferably from about 20 to about 30, weight percent based on the entire weight of the stabilizing composition.

Linear low density polyethylene is a low density polyethylene produced by a low pressure process, by Ziegler-Natta polymerization, or by use of the Phillips process. The low density is due to reduced crystallinity resulting from the use of up to about 10% of a 1-alkene comonomer such as 1-butene. The polymer contains short carbon chain side groups which reduce structural regularity and hence crystallization. LLDPE is used in such applications as film, pipe, rotational molding, injection molding, and wire and cable resins.

Regardless of the process used to produce the polymer, the operations associated with conversion of the dry product from the reactor into a form suitable for final processing for customer use are termed the finishing process. The finishing process may comprise stabilization, blending, extrusion, and pelletizing. The stabilizing composition useful in the method of this invention is produced in powder form, and is added at the pre-compounding stage to powdered polyethylene which is then pelletized.

The procedures employed to incorporate the stabilizing composition into the polyethylene are not critical and in general, the stabilizing composition can be readily incorporated into the polyethylene composition by conventional techniques for incorporating such additives into polyolefin resins. For example, the components of the stabilizing composition can be introduced into the polyethylene composition as a premix,

or the components can be maintained separately and added to the polyethylene composition simultaneously or sequentially, and then homogeneously distributed throughout the polyethylene composition by milling, extrusion blending, or some other mechanical working procedure.

Other additives can also be introduced into the polyethylene composition prior to, during and/or following addition of the stabilizing composition components. Such additives include other stabilizers, colorants, reinforcements, fillers, antistatic agents, lubricants, plasticizers, and the like.

The following examples are provided to illustratrate the present invention.

EXAMPLES

Comparative Examples A-K

Single component stabilizers and their effect on LLDPE Hunter "b" color and Melt Flow Index

In these examples, measurements were made of the melt-flow index of compositions containing (1) LLDPE; and (2) a single component of the stabilizing composition or a single organic monophosphite compound, which were subjected to repeated extrusions and evaluated according to ASTM Method D1238. In addition, molded plates were prepared from granules of the extruded polymer composition and used to determine Hunter 'b' color according to ASTM Standard D2244.

Each tested component of the stabilizing composition or each tested organic monophosphite compound, was dry blended into powdered LLDPE (gas phase Unipol type Linear

Low Density Polyethylene from Mobil Chemical Company) and stirred for sufficient time to ensure adequate dispersion of the additive and LLDPE. 500 ppm of zinc stearate, employed as an acid neutralizer, was then added to each mixture, to produce the test sample.

Each test sample was then pelletized by extrusion on a 3/4 inch extruder. The melt temperature and control zones on the extruder and die were adjusted to attain a melt temperature of 450°F.

Each pellet so formed was then rerun through the extruder five times to simulate multiple heat histories and promote degradation of the polymer. To limit the amount of sampling to a reasonable number, measurement of melt viscosity measurements were taken only on the first, third, and fifth passes through the extruder. The test samples having the best stabilization were affected the least; that is, the melt index values were consistant between the first, third, and fifth extrusions. The data for Comparative Examples A-K are presented in Table 1.

Color, or lack thereof, which is also an important property for extruded polymers of LLDPE, was measured by using a Hunter Colorimeter and measuring the change in the "b" value. As above for the melt viscosity measurements, measurement of color was taken only on the first, third, and fifth passes through the extruder.

As can be seen from the results in Table 1, the control sample (no additive), and test samples I and J had the lowest color values. However, the melt indices indicate a breakdown of the polymer since the values drop from 0.56 to 0.25 for the control, 0.87 to 0.5 for sample I, and from 0.84 to 0.45 for sample J. Comparative Example K, using only Ultranox 626, provided excellent color stability but the drop of the melt indices from 1.11 to 0.78 indicated a breakdown of the polymer.

Examples 1-21

Stabilization of LLDPE with 2- and 3-Component Stabilizer Compositions

In these Examples, two- or three- component compositions were evaluated for stabilization efficacy in LLDPE compositions. The classes of compounds used were hindered phenols, aromatic amines, and organic phosphites. The compounds used are commercially available and are known stabilizers for polyethylene polymers individually or in binary combinations. The data shown in Table 2 indicate the surprising improvements in stabilization efficiency using the stabilizing compositions useful in the method of this invention.

Samples were made and evaluated according to the procedures indicated above. A wide range of phenolic stabilizers were tested. The amine that was used, Naugard 445 (trademark, Uniroyal Chemical Company, Inc.), is 4,4'-bis (α, α-dimethylbenzyl)diphenylamine. Several phosphites were tested, but the best results, as seen in Table 2, were obtained using compositions comprising the pentaerythritol diphosphite, Ultranox 626 (trademark, GE Specialty Chemicals). Several phenolic compounds were tested with superior results, including Naugard 10, Naugard 76, and Naugard XL-1.

As can be seen in Table 2, superior results were obtained in Examples 3, 6, 9, 12, 15, 18 and 21, than were obtained in comparative Examples 1, 2, 4, 5, 7, 8, 10, 11, 13, 14, 16, 17, 19 and 20. It can be seen that the color is poorer in the comparative example blends comprising phenols and/or amine in combination with the organic monophosphites compared to the color in the corresponding blends comprising phenols and/or amine in combination with Ultranox 626.

These data clearly show the enhanced stabilizing

effect of a combination of a pentaerythritol diphosphite with an aralkyl-substituted diphenylamine and/or a sterically hindered phenol(s) compared to stabilization achieved with any material by itself, or compared to corresponding two- or three-component compositions comprising an organic monophosphite. This stabilizing effect is demonstrated by: 1) stable melt flow rates which indicate that the polyethylene is being protected from oxidative and thermal degradation; and 2) color stability. An objectionable change in color stability is indicated by increasing "b" values on the Hunter color scale. The lower the b value, the better the color stability.

TABLE I

COMPARATIVE EXAMPLES A-K SINGLE COMPONENT STABILIZERS

SAMPLE	FORMULATION	CONCENTRATION (PPM)	HUNTER "B" COLOR 5TH PASS	MELT INDEX PASSES 1	3	5
Control	Blank	-	1.8	0.56	0.37	0.25
A	NAUGARD-76	250	5.52	0.99	0.86	0.84
B	NAUGARD-76	500	6.91	1.03	0.99	1.02
C	NAUGARD-10	250	6.15	0.98	0.97	0.91
D	NAUGARD-10	500	7.27	1.06	1.14	1.14
E	NAUGARD-445	250	3.33	0.82	0.68	0.56
F	NAUGARD-445	500	3.99	0.87	0.76	0.67
G	NAUGARD-XL-1	250	8.59	1.01	0.96	0.95
H	NAUGARD-XL-1	500	9.65	1.11	1.15	1.15
I	NAUGARD-524	500	1.49	0.87	0.64	0.5
J	NAUGARD P	500	1.33	0.84	0.60	0.45
K	ULTRANOX-626	500	2.48	1.11	0.92	0.78

Notes for Table I: Naugard is a trademark of the Uniroyal Chemical Co.

The identities of the above compounds are as follows:

Naugard 76: Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate

Naugard 10: Tetrakis [methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] methane

Naugard 445: 4,4'-Bis (α,α-dimethylbenzyl) diphenylamine

Naugard XL-1: 2,2'-Oxamidobis [ethyl-3(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]

Naugard 524: Tris (2,4-di-tert-butylphenyl) phosphite

Naugard P: Tris (monononylphenyl) phosphite

Ultranox 626: Bis (2,4-di-tert-butyl) pentaerythriol diphosphite

TABLE 2
EXAMPLES 1-21: TWO AND THREE COMPONENT COMPOSITIONS

Sample	Formulation			Concentration (ppm)			Hunter "B" Color	Melt Index No. Of Passes		
	a)	b)	c)	a)	b)	c)	5th Pass	1	3	5
1	N-76	N-524		500	500		5.89	1.10	1.11	1.14
2	N-76	N-P		500	500		6.12	1.19	1.22	1.24
3	N-76	U-626		500	500		4.11	1.24	1.24	1.30
4	N-76	N-445	N-524	250	250	500	5.78	1.18	1.16	1.17
5	N-76	N-445	N-P	250	250	500	6.09	1.16	1.23	1.26
6	N-76	N-445	U-626	250	250	500	3.47	1.20	1.26	1.27
7	N-10	N-524		500	500		6.31	1.16	1.26	1.24
8	N-10	N-P		500	500		6.59	1.27	1.28	1.29
9	N-10	U-626		500	500		3.18	1.23	1.23	1.28
10	N-10	N-445	N-524	250	250	500	5.64	1.20	1.23	1.24
11	N-10	N-445	N-P	250	250	500	5.46	1.20	1.21	1.23
12	N-10	N-445	U-626	250	250	500	1.45	1.23	1.23	1.23
13	N-445	N-524		500	500		3.35	1.01	0.83	0.72
14	N-445	N-P		500	500		3.82	1.01	0.86	0.80
15	N-445	U-626		500	500		1.77*	0.95	0.93	0.94
16	N-XL-1	N-524		500	500		8.47	1.15	1.15	1.15
17	N-XL-1	N-P		500	500		9.0	1.22	1.21	1.16
18	N-XL-1	U-626		500	500		1.44*	0.95	0.95	0.96
19	N-XL-1	N-445	N-524	250	250	500	5.36*	0.97	0.96	0.97
20	N-XL-1	N-445	N-P	250	250	500	2.61*	0.96	0.97	0.95
21	N-XL-1	N-445	U-626	250	250	500	0.98*	0.95	0.96	0.94

Notes for Table 2: The abbrevation "N" stands for the word "Naugard" as was used in Table 1; likewise "U" stands for "Ultranox".

The samples marked with an * indicate that a different resin lot number was used.

WHAT IS CLAIMED IS:

1. A method for stabilizing a linear low density polyethylene (LLPDE) composition against degradation, which comprises incorporating into the LLPDE composition, an effective stabilizing amount of a stabilizing composition which comprises:

(a) a pentaerythritol diphosphite; and

(b) an antioxidant compound selected from the group consisting of:

(i) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; and

(ii) a combination of (i) and and at least one sterically phenol.

2. A method as recited in claim 1 wherein the pentaerythritol diphosphite is present in the stabilizing composition in an amount ranging from about 30 to about 70 weight percent.

3. A method as recited in claim 1 wherein the stabilizing composition comprises

a) a pentaerythritol diphosphite;

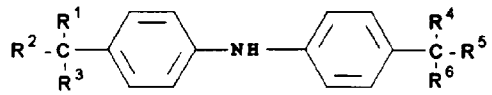
b) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; and

c) at least one sterically hindered phenol.

4. A method as recited in claim 3 wherein in the stabilizing composition, the diphenylamine is present in an amount ranging from about 10 to about 70 weight percent, the hindered phenol is present in an amount ranging from about 10 to about 70 weight percent, and the pentaerythritol diphosphite is present in an amount

ranging from about 30 to about 70 weight percent.

5. A method as recited in claim 1 wherein in the stabilizing composition, the diphenylamine has the formula



wherein R^1 and R^4 are hydrogen, C_1-C_4 alkyl or phenyl; and R^2, R^3, R^5 and R^6 are hydrogen or C_1-C_4 alkyl.

6. A method as recited in claim 1 wherein the stabilizing composition comprises

a) 4,4'-bis(α,α-dimethylbenzyl) diphenylamine;

b) a sterically hindered phenol selected from the group consisting of octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, tetrakis [methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] methane, and 2,2'-oxamidobis(ethyl)-3(3,5-di-t-butyl-4-hydroxyphenyl)propionate; and

c) bis (2,4-di-t-butylphenyl)pentaerthrytol diphosphite.

7. A LLPDE composition stabilized against degradation during mechanical processing by the presence therein of an effective stabilizing amount of a stabilizing composition comprising

(a) a pentaerythritol diphosphite; and

(b) an antioxidant compound selected from the group consisting of:

(i) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine;

and

(ii) a combination of (i) and at least one sterically hindered phenol.

8. A polyethylene composition as recited in claim 7 wherein the pentaerythritol diphosphite is present in the stabilizing composition in an amount ranging from about 30 to about 70 weight percent.

9. A polyethylene composition as recited in claim 7 wherein the stabilizing composition comprises

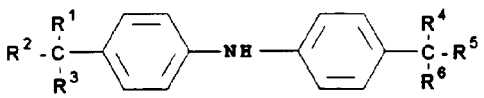
a) a pentaerythritol diphosphite;

b) at least one diphenylamine selected from the group consisting of alkyl-substituted diphenylamine and aralkyl-substituted diphenylamine; and

c) at least one sterically hindered phenol.

10. A polyethylene composition as recited in claim 9 wherein in the stabilizing composition, the diphenylamine is present in an amount ranging from about 10 to about 70 weight percent, the hindered phenol is present in an amount ranging from about 10 to about 70 weight percent, and the pentaerythritol diphosphite is present in an amount ranging from about 30 to about 70 weight percent.

11. A polyethylene composition as recited in claim 7 wherein in the stabilizing composition, the diphenylamine has the formula



wherein R^1 and R^4 are hydrogen, C_1-C_4 alkyl or phenyl; and R^2, R^3, R^5 and R^6 are hydrogen or C_1-C_4 alkyl.

12. A polyethylene composition as recited in claim 15 wherein the stabilizing composition comprises

a) 4,4'-bis(α,α-dimethylbenzyl) diphenylamine;

b) a sterically hindered phenol selected from the group consisting of octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, tetrakis [methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] methane, and 2,2'-oxamidobis(ethyl)-3(3,5-di-t-butyl-4-hydroxyphenyl)propionate; and

c) bis (2,4-di-t-butylphenyl)pentaerthrytol diphosphite.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 95/11447

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/18 C08K5/527 C08L23/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 274 200 (UNIROYAL) 13 July 1988 see page 2, line 30 - line 37 see page 2, line 49 - page 3, line 5 see page 7, line 26 - line 30 see page 8, line 11 - line 13	1-7,11
X	see claims 1-4,13	1-6

A	US,A,4 520 149 (M.D. GOLDER) 28 May 1985 see column 2, line 12 - line 35 see column 5, line 49 - line 59 see claims 1,3,8-13; examples	1,2,4-6

A	NL,A,8 403 880 (AKZO) 16 July 1986 see page 4, line 27 - page 5, line 29; claims 1,3,7; examples; table 2	1,2,5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 November 1995	15. 01. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Engel, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

.nformation on patent family members

Inte: nal Application No
PCT/US 95/11447

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-274200	13-07-88	AU-B-	594218	01-03-90
		AU-B-	8247687	16-06-88
		CA-A-	1326094	11-01-94
		DE-D-	3789011	17-03-94
		DE-T-	3789011	16-06-94
		ES-T-	2061515	16-12-94
		JP-B-	7013160	15-02-95
		JP-A-	63161043	04-07-88
		ZA-A-	8708398	11-05-88
US-A-4520149	28-05-85	CA-A-	1254333	16-05-89
		DE-A-	3474314	03-11-88
		EP-A,B	0144174	12-06-85
NL-A-8403880	16-07-86	NONE		